CHAPTER 7
SYNTHESIS AND CHARACTERIZATION OF SnS/ZnO NANOCOMPOSITE BY CHEMICAL METHOD

7.1 INTRODUCTION

SnS is a narrow band gap semiconductor material with a layered orthorhombic structure. It has both direct band gap (1.3 eV) and indirect band gap (1.0 eV) [28]. SnS is a potential material for solar cell applications, since the constituent elements are abundant. It provides no environment hazards and possess p-type conductivity. Solar cell application requires wide band gap n-type conductivity window material. In many solar cells, CdS has been used as a window material. For example, CdS/SnS heterostructure with conversion efficiency of 1.3% has been prepared by spray pyrolysis technique [9]. CdS/SnS solar cell with an efficiency of 0.22% has been prepared by chemical bath deposition method [144]. However, due to its toxicity, Cd free window material is required for the solar cell applications.

ZnO is a wide band gap semiconductor material with direct band gap of 3.37 eV and it has n-type conductivity. ZnO can be used as a window material in solar cells. Ichimura et al., have fabricated ZnO/SnS heterostructure by using electrodeposition technique with low conversion efficiency [10]. SnS/ZnO heterojunction has been fabricated by electrodeposition technique [74].

Complete details on the synthesis of SnS/ZnO nanocomposites are not available in the literature. In this chapter, SnS nanorods and SnS/ZnO
nanocomposite were synthesized by chemical method and their structural, morphological, vibrational and optical properties have been studied using XRD, TEM, MicroRaman and optical absorption measurements.

7.2 EXPERIMENTAL DETAILS

7.2.1 Synthesis of SnS Nanorods

SnS nanorods were synthesized by solvothermal method using SnCl₂.2H₂O and Na₂S as precursor in EG medium. After 10 minutes of stirring, the solution was transferred into teflon-lined cylinder and it was filled with EG upto 80% of its volume. Then, the closed chamber was kept inside a furnace at a temperature of 180 °C for 22 hours and then allowed to cool in air to room temperature. The black precipitates were centrifuged and washed several times using water and ethanol. The final products were dried at room temperature for 3 hours.

7.2.2 Synthesis of SnS/ZnO Nanocomposite

SnS/ZnO nanocomposite was synthesized by chemical route. To prepare SnS/ZnO nanocomposite, 0.1g of synthesized SnS nanorods were well dispersed in 20 ml of de-ionized water under magnetic stirring. 0.15 g of zinc acetate solution was prepared in 20 ml of de-ionized water. The prepared zinc acetate solution was added drop by drop into SnS solution. Finally, NaOH solution was added into the solution for the precipitation. The reaction was carried out at 80 °C for 3 hours. The precipitates were centrifuged and washed several times using water and ethanol. The final products were dried at room temperature for 2 hours.
7.3 RESULTS AND DISCUSSIONS

7.3.1 Structural Studies

Figure 7.1(a) shows the XRD pattern of SnS nanorods. All the diffracted peaks of SnS nanorods are indexed to orthorhombic structure.

![XRD patterns](image)

**Figure 7.1** XRD patterns of (a) SnS nanorods synthesized at 180 °C for 22 hours and (b) SnS/ZnO nanocomposite.

This is in good match with the standard JCPDS card NO: 39-0354. Impurity peaks such as SnS₂, SnO₂ are not observed in the synthesized sample. The XRD pattern of SnS/ZnO nanocomposite is shown in the Figure 7.1(b). It shows both orthorhombic
structure of (39-0354) SnS and wurtzite structure of (36-1451) ZnO, which confirms the formation of SnS/ZnO nanocomposite. The intensity of diffracted peaks of SnS is decreased in the SnS/ZnO nanocomposite compared to that of pure SnS nanorods. This may be due to coating of ZnO nanoparticles on the surface of SnS nanorods. A less intensity peak at 33.5° is observed in the XRD pattern of SnS/ZnO nanocomposite and it is corresponding to the cubic structure of ZnO (JCPDS card NO: 65-2880).

Figure 7.2 (a) shows the TEM image of SnS nanorods prepared at temperature of 180 °C for the reaction time of 22 hours. The average diameter of the SnS nanorods is about 85 nm and length is in several micrometers. The HRTEM image shown in Figure 7.2 (b) indicates single crystalline in nature of SnS nanorods. Figure 7.2 (c) shows the TEM image of SnS/ZnO nanocomposite. The average particle size of ZnO nanoparticle is about 12 nm. TEM image of SnS/ZnO nanocomposite shows that the ZnO nanoparticles are coated on the surface of SnS nanorods and confirms the formation of SnS/ZnO nanocomposite. Figure 7.2 (d) shows the corresponding HRTEM.
Figure 7.2 (a) TEM image of SnS nanorods, (b) corresponding HRTEM image, (c) TEM image of SnS/ZnO nanocomposite and (d) corresponding HRTEM image.
Figure 7.3 (a) EDX spectrum of SnS nanorods and (b) EDX spectrum of SnS/ZnO nanocomposite.

Figure 7.3 (a, b) shows the EDX spectra of SnS nanorods and SnS/ZnO nanocomposite respectively. Figure 7.3 (a) confirms the formation of SnS nanorods. In addition, tin and sulfur atoms, zinc and oxygen atoms are present in Figure 7.3 (b). It confirms the formation of ZnO nanoparticles in SnS/ZnO nanocomposite.

Figure 7.4 shows schematic representation of synthesis of SnS/ZnO nanocomposites. The ZnO nanoparticles were attached on surface of SnS nanorods by precipitation of ZnO using zinc acetate and sodium hydroxide as precursor and precipitating agent respectively at 80 °C.
Figure 7.4 Schematic representations for the formation of SnS/ZnO nanocomposite.

7.3.2 Optical Studies

The room temperature MicroRaman spectrum of SnS nanorods is shown in the Figure 7.5. The Raman modes for SnS nanorods are observed at 95.5 cm$^{-1}$, 164 cm$^{-1}$, 191.4 cm$^{-1}$ and 219 cm$^{-1}$. Based on the Raman spectra of SnS single crystal, the observed Raman modes for SnS nanorods at 95.5 cm$^{-1}$ and 219 cm$^{-1}$ are assigned to the $A_g$ mode, the mode observed at 164 cm$^{-1}$ is assigned to $B_{3g}$ mode and the mode observed at 191.4 cm$^{-1}$ is assigned to $B_{2g}$ mode [105, 145]. The $B_{3g}$ mode observed at 164 cm$^{-1}$ is prominent in SnS nanorods whereas, in the case of Raman spectra of single crystal the intensity of $B_{3g}$ mode at 164 cm$^{-1}$ is weak [145].
Figure 7.5 MicroRaman spectrum of SnS nanorods prepared at 180 °C for 22 hours.

The MicroRaman spectrum of SnS/ZnO nanocomposite is shown in the Figure 7.6. The Raman modes for SnS/ZnO nanocomposite are observed at 193.5 cm⁻¹, 375.5 cm⁻¹, 434.4 cm⁻¹, 483 cm⁻¹, 542 cm⁻¹ and 636 cm⁻¹. The mode observed at 193.5 cm⁻¹ is assigned to $B_{2g}$ mode of SnS nanorods [145]. The intensity of $B_{2g}$ mode dramatically decreased in the case of SnS/ZnO nanocomposite compared to $B_{2g}$ mode of pure SnS nanorods. This indicates the surface of SnS nanorods are coated with small size ZnO nanoparticles. The modes observed at 375.5 cm⁻¹, 434.4 cm⁻¹, 483 cm⁻¹ and 542 cm⁻¹ are assigned to $A_{1}TO$, $E_{2}$ (high), $2LA$
and B₁ (high) modes of ZnO nanoparticles [146]. Apart from SnS and ZnO modes an additional mode observed at 636 cm⁻¹, which is assigned to A₁g mode of SnO₂ [147]. This might be due to small amount of SnO₂ impurity present in the sample.

The optical absorption spectrum of SnS nanorods prepared at 180 °C for 22 hours is shown in the Figure 7.7. SnS nanorods shows both direct and indirect band gaps at 914 nm (1.35 eV) and 1021 nm (1.21 eV) respectively. Quantum confinement related shift is not observed in the absorption spectrum of SnS.

**Figure 7.6 MicroRaman Spectrum of SnS/ZnO Nanocomposite.**
nanorods. This may be attributed to the larger value of the diameter and length of the nanorods when compared to the exciton Bohr radius of SnS (7 nm) [65]. The optical absorption spectrum of SnS/ZnO nanocomposite is shown as inset in Figure 7.7 and it indicates an absorption in the visible region.

Figure 7.7 UV-VIS-NIR Absorption Spectra of SnS nanorods and the optical absorption spectrum of SnS/ZnO nanocomposite is shown as inset.
7.4 CONCLUSIONS

SnS nanorods and SnS/ZnO nanocomposite were synthesized by chemical method. From the XRD pattern, the structure of SnS and ZnO were identified as orthorhombic and wurtzite respectively. The microRaman spectrum of SnS/ZnO nanocomposite shows modes related to SnS and ZnO and the intensity of the $B_{2g}$ mode of SnS decreased dramatically since the surface of the SnS nanorods were coated with ZnO nanoparticles. The optical absorption spectrum of SnS nanorods showed direct and indirect band gap transitions at 1.35 eV and 1.21 eV respectively. The optical absorption spectrum of SnS/ZnO nanocomposite shows absorption in the visible region.